Modification of Carbon Paste Electrode Based on Molecularly Imprinted Polymer for Electrochemical Determination of Diazinon in Biological and Environmental Samples

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Abstract: The wide use of pesticides can lead to environmental and human adverse effects. Diazinon, as an organophosphorous pesticide, is used in agriculture because of its low cost and high efficiency on insects. Due to the increasing application of pesticides, accurate analytical methods are necessary. The aim of this work was modification of carbon paste electrode composition and applying it as a sensor for determination of diazinon in biological and environmental samples. Multi-walls carbon nanotubes and a molecularly imprinted polymer were used as modifiers in the sensor composition. A molecularly imprinted polymer and a non-imprinted polymer were synthesized for applying in the electrode. After optimization of electrode composition, it was used to determine the analyte concentration. Instrumental parameters affecting the square wave voltammetric response were adjusted to obtain the highest current intensity. The modified electrode with MIP showed very high recognition ability compared to the electrode containing NIP. The obtained linear range was 5×10^{-10} to 1×10^{-6} mol L^{-1}. The detection limit of the sensor was 1.3×10^{-10} mol L^{-1} and the relative standard deviation for analysis of target molecule by the proposed sensor was 2.87%. This sensor was used to determine the diazinon in real samples (human urine, tap, and river water samples) without special sample preparation before analysis. The optimization of electrode composition containing mentioned modifiers improved its response considerably.

Keywords: Diazinon · Molecularly Imprinted Polymer · Voltammetric Sensor · Modified Carbon Paste Electrode · Biological Monitoring

1 Introduction

Pesticides are natural or synthetic substances used to control or repel pests. They are very important group of environmental pollutants with heterogeneous toxicity and their emission can occur during formulation, production, use, and disposal. The multi-route exposure of humans to pesticides can cause different adverse effects. They may also enter to soil, waters, and foods via different ways. Organophosphate compounds, as the most widely used pesticides worldwide, can be immunotoxic, cytotoxic, and genotoxic. Diazinon (O,O-diethyl O-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl] phosphorothioate), as an organophosphorus insecticide, is used to control insects in soil, on plants, fruits, and vegetables. Diazinon is an anti-cholinesterase compound that inhibits cholinesterase, an enzyme essential for the function of central nervous system. Also, diazinon, at high doses, can cause nausea, dimness of vision, muscle tremors, and difficult breathing. It can cause adverse effects on gastrointestinal tract, skin, lungs, and nervous system [1–6].

Because of the increasing application of pesticides, there is a need for their environmental and biological monitoring to assess the environmental pollution, occupational exposure under working conditions, and public exposure due to domestic and urban usage of these compounds [7]. Human biomonitoring, a critical component of occupational health, is a useful tool to assess the exposure to low levels of chemicals. In this regard, developing

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the new sensitive and accurate procedures allows the reliable, easy to use, and cost effective assessment [8].

A number of analytical methods have been reported to determine the pesticides, such as liquid chromatography and gas chromatography with electron capture detection with very low detection limits. Other determination methods employed for the analysis of these compounds are spectrophotometry [9,10], immunoassay [9], infrared spectroscopy [11], or enzymatic techniques [12] sometimes in combination with mass spectrometry (MS) [13], or the flow injection technique [9,14]. Due to some problems, the issue of pesticide residue analysis is still a critical subject in analytical chemistry; therefore, developing novel, simple, and inexpensive analytical methods should be taken into account to determine the pesticides. These problems include: the mentioned techniques are very expensive and the level of personnel, laboratory equipment, and expertise required for them is considerable. The need for pesticide analysis is greater in developing countries because of the agrarian basis of them; however, the MS instrumentation is so expensive for wide usage. A sample pretreatment step is needed to determine the analytes at trace levels in complex matrices. And due to an increasing number of samples, speeding the analysis and shortening of the analytical run times are required. Therefore, during the last few years, improving the novel analytical techniques in term of sensitivity, selectivity, and precision have been considered for the determination of trace analytes in different complex matrices like environmental and biological samples [7,15–17, 18].

Sensors, as the miniaturized instruments, are the appropriate and interested devices to monitor the trace and even ultra-trace pesticides. They are highly qualified tools for on-site monitoring due to suitable size, portability, and low cost. Modified electrodes are being used in the electrochemical determination of many compounds. Molecular imprinted polymers (MIPs) can be used as recognition elements or modifying agents in sensors structure to increase their selectivity [19–23]. A MIP is a high selective synthetic receptor with molecular adsorption sites that serves high specificity and selectivity for analyte of interest. This polymeric receptor is favorable because of mechanical, thermal, and chemical stabilities [24–26]. The characteristics of the prepared polymer are dependent on some parameters like functional monomers, initiator, porogenic solvent, and the ratio of monomer to cross-linker. Therefore, consideration must be given to the selection of these parameters in order to synthesize an optimal polymer with high affinity capacities [27–30].

An electrode modified with a MIP, as the sensing system, can meet some important characteristics such as high sensitivity and selectivity, portability, analytical response, and long life time. Recently, the modification of electrode by different agents like MIPs and nano structures has led to significant advances in quantification of analytes because of their great properties [26,31–33]. Modified electrodes may be used in combination with different electrochemical techniques like potentiometry, differential pulse voltammetry (DPV), differential pulse polarography (DPP), and adsorptive stripping voltammetry (AdSV) to analyze the environmental and occupational samples [34–35]. The aim of this study was to optimize the composition of carbon paste electrode modified with MIP and MWCNTs in order to introduce a novel and easy-to-use electrochemical sensor for selective and sensitive determination of diazinon pesticide in environmental and biological samples.

2 Experimental

2.1 Instruments and Reagents

Electrochemical analyses were performed by a three-electrode system using an AUTOLAB PGSTAT302. The FTIR (Perkin Elmer) spectroscopy was used as an imaging system. The modified sensors containing MIP or NIP were used as working electrodes. An Ag/AgCl electrode and a graphite rode were chosen as the reference and counter electrodes, respectively. Methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Fluka (Buchs, Switzerland). Diazinon (Sigma–Aldrich), Paraffin oil (Merck) and 2,2-azobisisobutyronitrile (AIBN) from Sigma–Aldrich (Munich, Germany) were used. Multi-Wall Carbon Nano Tubes (MWCNTs) were provided from Research Institute of the Petroleum Industry (Iran). Graphite powder (1–2 μm particle size) and all other chemicals in analytical grade were purchased from Merck (Germany).

2.2 Preparation of the Molecularly Imprinted Polymer (MIP)

To conduct the non-covalent imprinting approach for synthesis of MIP, the diazinon template (1 mmol) was dissolved in 10 mL of chloroform, containing MAA monomer (6 mmol), EGDMA (20 mmol) as cross-linker, and AIBN (60 mg) as initiator. The solution was sealed and purged with nitrogen for 10 min. Then, the glass tube containing the polymer mixture was placed in a water bath at 60° overnight. After polymerization, the obtained MIPs were dried and grounded. Then, template molecules were removed by extensive washing via Soxhlet extraction in methanol for 48 h several times. Finally, the particles were dried under vacuum at 60°. Figure 1 showes the scanning electron microscope (SEM) image of prepared molecularly imprinted polymers for diazinon. The scanning electron microscopy was done for total investigation of the MIP morphology. According to the observations, the formation of diazinon imprinted particles has been successfully performed and there is a spherical shape with a narrow size distribution.

The non-imprinted polymer (NIP) was prepared in the same condition, except for addition of the template molecule to the mixture.

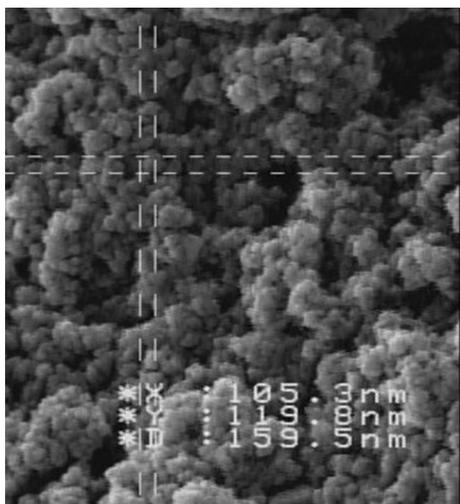In addition, FT-IR spectroscopic analysis of unleached and leached diazinon imprinted polymer materials

Fig. 1. SEM image of prepared molecularly imprinted polymers.

(Fig. 2) indicates the similarity in molecular structure of these polymers. As it can be seen, the carboxylic acid O-H Stretch vibration in the washed and unwashed MIPs are 2959 and 2967 cm^{-1}, respectively. This displacement toward lower frequencies can be attributed to the interaction of hydrogen with diazinon in the unwashed MIP. The carbonyl group C=O stretching peak was observed in 1737 and 1727 cm^{-1}, for washed and unwashed polymers, respectively and they may be related to MAA and EGDMA.

The displacement of these peaks and the other ones in both polymers confirm the interaction between functional monomer and template molecule. The peaks beyond 1500 cm^{-1}, placed in the fingerprint region, are complicated to interpret due to many bands overlapping each other.
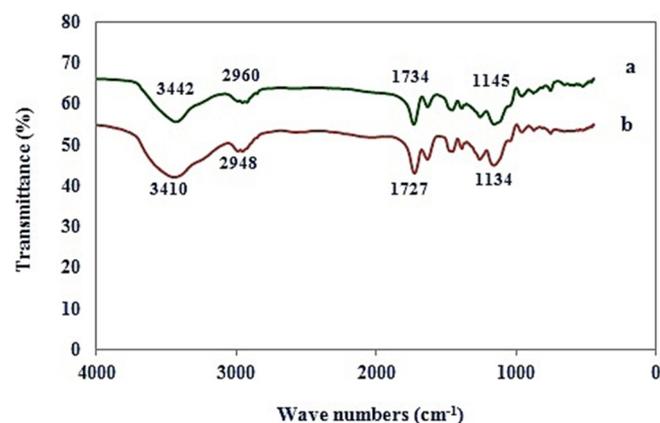

Fig. 2. Infrared spectra of the washed (a) and unwashed MIP particles (b).

2.3 Preparation of the Electrode

The bare carbon paste electrode (CP) was prepared by hand mixing of graphite powder and paraffin oil at a ratio 75:25 (w/w%). The mixture was homogenized in a mortar for at least 10 min. The final paste was packed into a tube (id: 3 mm, paste deep: 1 cm) in which electrical contact was provided by a copper wire. The total weight of the paste was considered 0.1 g and its composition percentages calculated based on this weight. The modified electrodes were prepared in the same procedure by mixing 55% graphite, 25% paraffin oil, 15% MIP, and 3% MWCNTs (electrode No. 5 in Table 1). As it can be seen in Table 1, different percentages of graphite, MWCNT, paraffin oil, and MIP or NIP were used for preparing all eleven electrodes. Then, the electrode surface was polished using a paper to remove the excess of material. To survey the role of each added component for improvement of the electrode response, several electrodes containing different percentages of components were prepared.

2.4 Electrochemical Analysis

The procedure used to obtain square wave voltammograms for diazinon was done according to the following steps:

Extraction step: each prepared electrode was inserted into the diazinon solution with defined concentration and its pH was adjusted using hydrogen chloride (pH: 3). The pH factor was optimized in the range of 2 to 8 for selecting the optimum one. All solutions were stirred for 15 minutes at stirring rate 600 rpm.

Determination step: The electrochemical cell containing supporting electrolyte (acetate buffer 0.1 mol L^{-1}, pH: 4) was used for voltammetry experiments. At first, a constant deposition potential (0.8 V) was applied to the electrode for 100 s, then, the potential was scanned in defined range. The application of deposition potential for proper time leads to the accumulation of analyte on the surface of the modified electrode, causing the more sensitivity of the electrode during electrochemical analysis. The highest current intensities were obtained in amplitude 0.15 V, frequency 50 Hz, and step potential 0.05 V. It is worth mentioning that factors affecting the extraction of analyte and instrumental parameters were selected based on some experiments to obtain the maximum peak current. In fact, parameters of the extraction pH, stirring rate of solution, extraction time, analysis pH, deposition potential and its exertion time, electrolyte concentration, square wave amplitude and frequency had been previously optimized in different levels and the selected parameters were used in this study. For example, the exertion of deposition potential of 0,8 V to the working electrode for 100 s caused increasing the current intensity due to the accumulation of analyte into the electrode surface.

2.5 Preparation of Solutions

The stock solution of 1×10^{-2} mol L^{-1} diazinon was prepared in ethanol and used for further dilutions by deionized water to provide working solutions. In order to assess the possibility of diazinon determination in real samples, unexposed biological and environmental samples consisted of urine, tap, and river samples were considered. There was no need for special preparation procedures for these samples. Only urine samples were diluted 1:3 with deionized water for avoiding the probable adsorption of interferences on the surface of electrode. The specified amount of diazinon was spiked in all solutions to do the voltammetric analysis. The modified working electrode (MIP-CP) was placed in the solutions for 15 min to extract the diazinon. Then, the measurement was completed in the analyzing step via inserting the electrode into an electrochemical cell with mentioned characteristics. After applying the deposition potential, square wave voltammograms were recorded in the scan range of -1.2 to 0.0 V.

3 Results and Discussion

3.1 Electrochemical Behaviour of Diazinon

To select the best potential scanning range for diazinon, its cyclic voltammetric behaviour was investigated by a bare carbon paste electrode. The potential was swept in a wide interval (-1.5 to $+1.5$ V) to find the proper scan range. The scanning showed a reduction process and a sharp cathodic reduction peak in acidic supporting electrolyte appeared at around -0.6 V. Therefore, this peak was chosen for all later square wave voltammetric experiments. As expected, the SWV response of diazinon on the CP electrode showed a reduction signal at around the selected potential. Figure 3 indicates the cyclic voltammogram of diazinon.
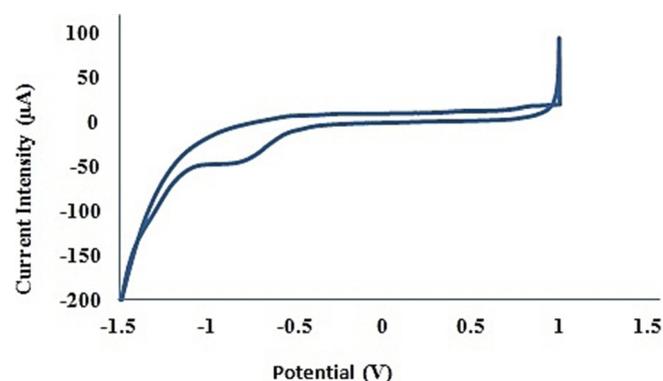

Fig. 3. Cyclic voltammetry (scan rate: 100 mV s^{-1}) behavior of diazinon at the surface of bare carbon paste electrode.

3.2 Optimization of Carbon Paste Electrode Composition

The base of carbon pastes is usually a mixture of powdered graphite and binder. To study the effects of modification on electrode performance, the carbon paste was modified with other components as modifying agents.

In this study, the multi-wall carbon nanotubes (MWCNTs) and MIP were used as modifiers. Since the type and ratio of applied components are important to have the optimum construction, different amount of modifiers were added to paste and they were packed into the electrode tube. In order to exact comparison, 11 electrodes were prepared. The bare carbon paste electrode and the electrode modified with NIP were also considered. The electrochemical experiments were carried out by various prepared CPEs to survey the role of modifiers and their ratio in the improvement of electrode response. Table 1 shows the responses of different electrode compositions in the similar electrochemical conditions. Given the findings, both the modifier type and its amount play the significant role in this respect.

Peak currents obtained with electrodes containing MWCNTs increased due to these nanoparticles properties such as vast surface area, high electrical conductivity, and proper chemical stability. Using this modifier in the paste inhances the sensor conductivity and the rate of transduction of the chemical signal to electrical signal. Therefore, the application of carbon nanotubes in electrochemical measurements can lead to desired sensors with appropriate characteristics. The constant percentage of this modifier was selected based on previous studies [36–37]. Furthermore, using MIPs in the carbon paste electrodes is a promising approach toward the development of biomimetic sensors. Such modified electrodes offer new tools to overcome some limitations of biosensors. The intrinsic properties of MIPs such as high selectivity to the molecule of interest, mechanical and chemical stability, ease of preparation, application in harsh environments and their durability have made them attractive for using as recognition elements in sensor structure. Many of literatures prove the growing usage of MIPs for sensing purposes [38,39]. As it can be seen in Table 1, the highest peak current is related to carbon paste modified with two modifiers. Therefore, the CPE modified with both MIP and MWCNTs can be considered as a novel sensor for selective determination of the target molecule. In addition, the percentage of MIP in paste composition is effective on electrode response. According to results, the paste containing 15 % MIP has the highest efficiency to adsorb the analyte and it was selected as the optimum one (electrode No. 5). Using higher percentage of MIP leads to the reducing of the electrode response due to the increasing of resistance of the paste. Alizadeh et al. used 12 % MIP in the composition of carbon paste sensor based on a biomimetic molecular imprinted polymer for voltammetric determination of ultra-trace promethazine. In the optimized MIP percentage, increasing the selective sites in the electrode surface led to the improvement of the elec-

Table 1. The optimization of carbon paste composition for determination of diazinon ($5 \times 10^{-7}\,mol\,L^{-1}$)

Electrode No.	Composition of Carbon Paste (Wt. %)					Voltammetric Response (µA)
	Graphite Powder	Binder (Paraffin oil)	MWCNTs	MIP	NIP	
1	75	25	0	0	0	11.82 ± 2.9
2	72	25	3	0	0	24.38 ± 3.5
3	60	25	0	15	0	36.85 ± 2.8
4	62	25	3	10	0	41.44 ± 2.6
5	**57**	**25**	**3**	**15**	**0**	**58.04 ± 2.2**
6	50	25	3	22	0	43.52 ± 3.2
7	45	25	3	27	0	34.22 ± 1.7
8	62	25	3	0	10	25.43 ± 2.1
9	57	25	3	0	15	31.02 ± 3.3
10	50	25	3	0	22	23.31 ± 2.2
11	45	25	3	0	27	19.11 ± 2.1

trode response. Decreasing the electrode signal in higher percentage of MIP could be probably related to the insulating effect of the MIP particles. [40].

3.3 Effect of Interferences

To assess the matrix effect on the selectivity of suggested MIP-CP sensor, the electrode was inserted into the solutions of diazinon as well as some ions and commonly used pesticides. At first, for studying the probable interference of each pesticide with the diazinon peak position, the experiments were separately performed for two defined concentrations. By the instrumental parameters adjusted for voltammetric determination of diazinon, other pesticides had no interferences in this respect. Their peaks appeared in other positions of the scanning range or no peak was seen in existing conditions. After that, the response of sensor was recorded for diazinon in simultaneous presence of different concentrations of ions and pesticides. In this case, the concentration of diazinon was constant ($1 \times 10^{-7}\,mol\,L^{-1}$). Table 2 indicates the response of MIP-CP electrode for each test. The 1000-fold excess

Table 2. The response of suggested sensor for diazinon in the presence of various ions and pesticides

Tested compounds	MIP-CP Response	
	I (µA) ($5 \times 10^{-7}\,mol\,L^{-1}$)	I (µA) ($1 \times 10^{-7}\,mol\,L^{-1}$)
Coumachlor	5.2	N.D
Dicloran	N.D	N.D
Dimethoate	9.4	5.3
Dichlrofention	7.7	4.2
Diazinon	**61**	**26.2**
Diazinon (in simultaneous presence of other pesticides)		
100-fold	–	23.9
500-fold	–	24.3
1000-fold	–	23.1
Diazinon (in simultaneous presence of ions)		
300-fold	–	25.1
700-fold	–	24

of coumachlor, dicloran, dichlrofention, and dimethoate pesticides in target solution could not interfere with respect to the diazinon peak current. Also, cadmium, calcium, magnesium, lead, and nitrate ions were gradually added to the defined concentration of diazinon. Given the findings, the mentioned ions had no interfering effect on analyte signal till 700-fold concentration. Clearly, the modified electrode with MIP was very selective for diazinon, so that, other compounds showed the negligible responses compared to that. These findings affirm the ability of modified electrode to interact strongly with the target analyte due to the existence of specific sites for that in the MIP structure.

3.4 Comparison of the Prepared MIP and NIP

After optimization of electrode composition for determination of diazinon, the difference between responses of electrode No. 5 and electrode containing the same amount of NIP (electrode No. 9) was studied. Both of them were also compared with the bare carbon paste electrode. According to the findings, there was significant difference ($P < 0.05$) between these polymers to adsorb diazinon molecules, affirming the formation of selective adsorption sites in the MIP structure. Fig 4 indicates the square wave voltammograms related to determination of defined concentration of diazinon by MIP-CP and NIP-CP.

3.5 Method Validation

The proposed modified electrode was successfully applied as a working electrode and, as it was mentioned before, it had acceptable performance for detection of diazinon in the simultaneous presence of other molecules and ions. Therefore, the prepared MIP-CP sensor was used to plot the calibration curve. The tested concentration interval was from 1×10^{-10} to $1 \times 10^{-4}\,mol\,L^{-1}$. To plot the calibration curve, the sensor was subjected

to the diazinon solutions with different concentrations and then, the voltammogram related to each solution was recorded. The linear relationship between the peak cur-
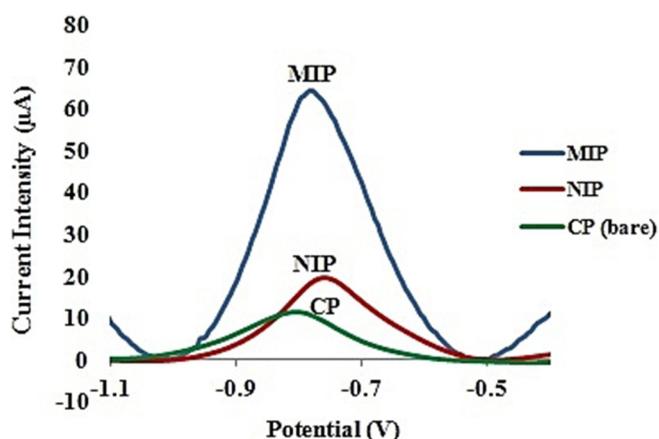
Fig. 4. The voltammograms of MIP-CP, NIP-CP, and CP for defined concentration of diazinon (5×10^{-7} mol L^{-1}).

rent and diazinon concentration was obtained over the range of 5×10^{-10} to 1×10^{-6} mol L^{-1}. Since the higher linearity of calibration curve in lower concentrations is important for accurate analysis of the trace amount of analyte, this curve was drawn in two concentration regions with R^2 of 0.998 and 0.999 (Fig 5). In the highest concentration range, the sensor response was not linear due to the limitation of available binding sites in the MIP. The lowest detectable concentration (LOD) and the lowest quantitative concentration (LOQ) were 4.1×10^{-10} and 1×10^{-9} mol L^{-1}, respectively. The LOD and LOQ were calculated using related equations, as follow. In addition, the
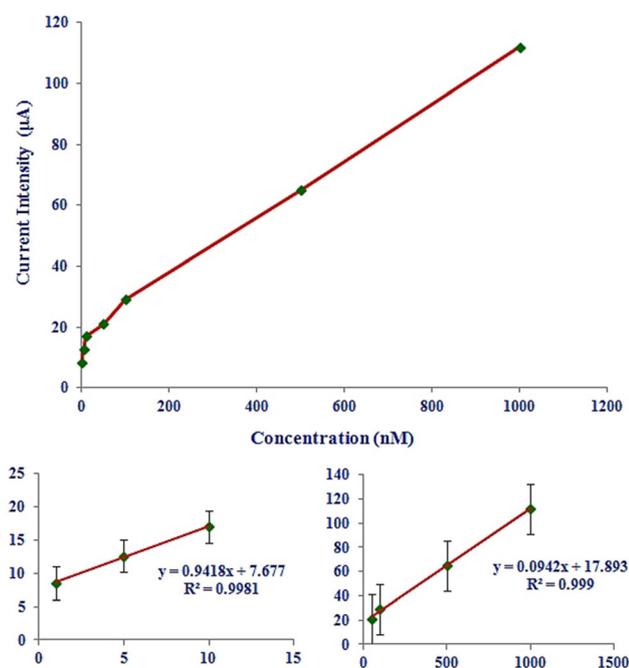
relative standard deviation (RSD) for five replicate experiments was calculated to be 2.87 %.

$$LOD = \frac{3Sb}{m} \quad LOQ = \frac{10Sb}{m}$$

where, s_b is the standard deviation of the blank and m is the slope of calibration graph.

In fact, using the nano-composite sensor based on MIPs achieved a lower detection limit in comparison with other studies in which there were no modified electrodes. Guziejewski et al. [41] obtained the detection limit of 1.1×10^{-8} by applying the square wave adsorptive stripping voltammetric for determination of diazinon [34]. It seems that the better LOD of designed electrode can be attributed to the higher affinities of the recognition sites of this MIP based electrode.

To determine the reproducibility of the electrochemical sensor, required experiments were considered using day to day and within a day method. In this regards, six measurements in six consecutive days, as well as six measurements within one day were performed. The coefficient variations (CV) for day to day and within day experiments were 4.05 % and 3.16 %, respectively. Statistically, it demonstrates the satisfactory performance of the chemically modified electrode for diazinon determination. In addition, the long-term stability of the proposed sensor was evaluated in a period of one month. No significant change of peak current was observed and the sensor retained 95.28 % of its initial response.

3.6 Determination of Diazinon in Spiked Urine and Real Water Samples

To investigate the applicability of the modified carbon paste electrode to real samples, it was applied for residue determination of diazinon in urine and water samples. Because real urine samples encountered diazinon were not available, synthetic samples prepared by spiked method were used. All the real sample analyses were done by the procedure explain in section 2.3 using standard addition method. There was no need for digestion or other special pre-treatment steps prior to the voltammetric analysis due to the extraction step and the electrochemical determination step which were totally separated Different amounts of diazinon were added to the urine and water samples, then, the electrodes were dipped into the sample solutions. Left till the diazinon molecules were extracted on the electrodes surfaces and then pulled out, washed, and analysed in buffer solution through voltammetric procedure. Finally diazinon recoveries were calculated. Table 3 shows the results obtained for recovery of diazinon in spiked samples. As it can be seen, the proposed electrode in combination with voltammetry procedure is sufficiently acceptable for environmental and biological monitoring of diazinon. It is worth mentioning that, the modern analytical tools help reduce or eliminate the sample preparation steps as one of the most time-con-

Fig. 5. Calibration curve plotted for voltammetric determination of diazinon with MIP-CP.

Table 3. The performance of the modified sensor in spiked real samples

Sample	Added (ng/ml)	Found (ng/ml)	RSD (%) (n=3)	Relative Recovery (%)
	–	N.D	–	–
Tap Water	20	18.80	3.12	94.00
	200	193.00	2.91	96.50
	2000	1909.00	2.06	95.45
	–	< 0.2	4.21	–
River Water	20	19.50	2.44	97.50
	200	190.00	1.76	95.00
	2000	1881.00	2.83	94.05
	–	< 0.2	–	–
Urine	20	18.40	3.61	92.00
	200	186.00	2.77	93.00
	2000	1848.0	3.11	92.4

suming, tedious, and error-prone aspects prior to chemical analysis. The proposed novel sensor provides a fast, simple, sensitive, and inexpensive tool for determination the analyte in complex matrices with no need for special preparation steps.

3.7 Comparison of the Proposed Sensor with Literatures

The proposed method was compared with other reported methods to determine diazinon in different samples. As it can be seen in Table 4, the LOD provided by the introduced sensor is clearly better than other studies. The use of both MIP and MWCNTs in the composition of sensor has resulted in very low detection limit of the sensor.

4 Conclusions

In this work, a novel modified sensor was proposed for the rapid detection of trace levels of diazinon in environ-

Table 4. Comparison between proposed method and other literatures foe determination of diazinon

Studied Samples	Method	LOD (µg/L)	Ref.
diazinon insecticidal formulations	Square wave adsorptive stripping voltammetry by hanging mercury drop electrode	3.3	41
surface water	Gas Chromatography-Mass spectroscopy (GC-MS)	0.08	42
lake water	Voltammetric method and Nafion-coated glassy carbon electrode	22.8	43
rat plasma and urine samples	High-performance liquid chromatographic (HPLC)	100	44
well water and fruits	Voltammetric method by carbon paste electrode modified with MIP	0.24	45
tap and river water and in urine samples	Voltammetric method by carbon paste electrode modified with MIP and MWCNTs	0.039	This study

mental and biological samples. Using MIPs and nano structures in the composition of carbon paste is considered in the modern analytical chemistry. The selectivity of an analytical method is a critical factor. Therefore, it is important the selectivity and resolution of methods to detect the analytes in complex matrices when developing the new methods. In this respect, modified sensors as the fast, simple, sensitive, and inexpensive tools help to selectively detect the specific compounds. The MWCNTs enhance the sensor responses due to increasing of the electrode surface area, as well as improving the electron transfer between the electrode and the supporting electrolyte. The presence of MIPs can greatly increase the selectivity of the electrode. In this regard, the suggested sensor was successfully applied for detection of diazinon in real samples with no special sample pretreatment steps.

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